Oxide/water interfaces: structure, dynamics, chemical reactivity and pKa acidities from DFT-based MD simulations

Marie-Pierre Gaigeot

Marialore Sulpizi, Michiel Sprik,
A. Motta, Dominique Costa

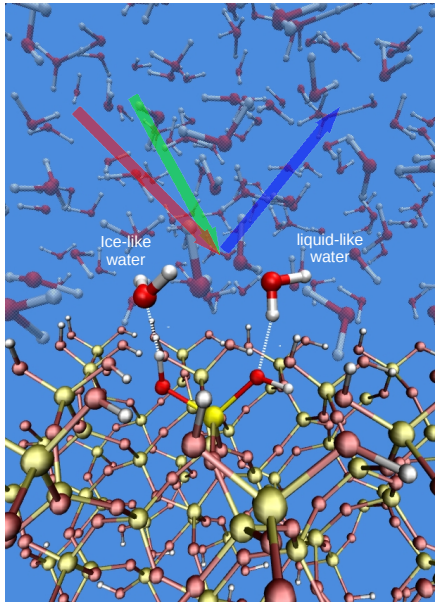
ATIGE

LAMBE Laboratoire Analyse et Modélisation
pour la Biologie et l'Environnement - UMR 8587 CNRS
Université d'Evry val d'Essonne - Paris France

IUF Institut Universitaire de France
Overseas Fellow @ Churchill College Cambridge-UK

mgaigeot@univ-evry.fr
http://mpgaigeot-research.fr

Motivations : VSFG Spectroscopy at oxides/water interfaces



- VSFG : Vibrational Sum Frequency Generation, non-linear spectroscopy

  VSFG : sensitive to interface species only (inactive in pure liquids)

  VSFG exps : O-H intramolecular stretching motions probed

  VSFG : water layers probed

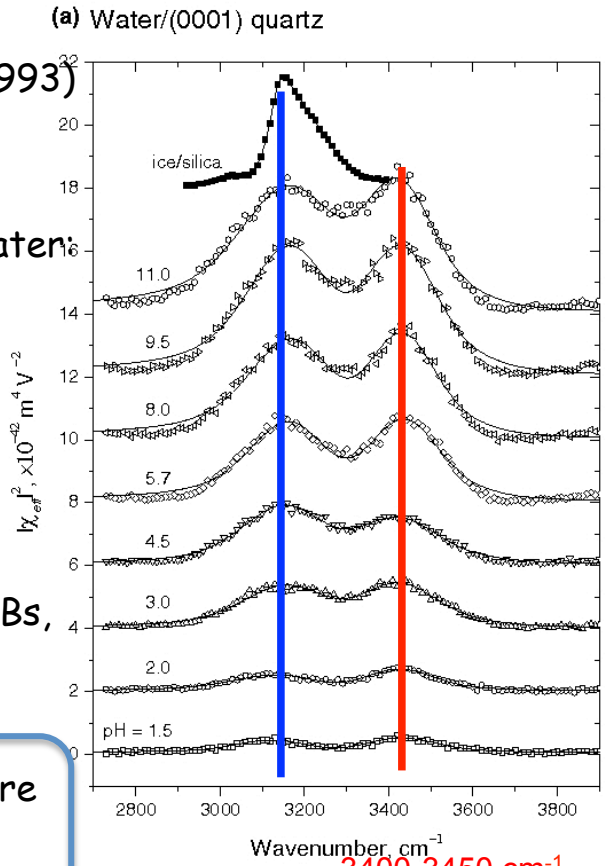
- Exps developed Shen et al. (USA, PRL 1993)

- Debated assignments in literature in terms of different organisation of water:
  - «Liquid-like» *vs* «Ice-like» water
  - Water: adjacent/subsequent layers to surface
  - 4-coordinated *vs* under-coordinated water

- What does « liquid/ice-like » mean ? Water-surface Hbonds formed, strong/weak HBs, but can we be more specific ?

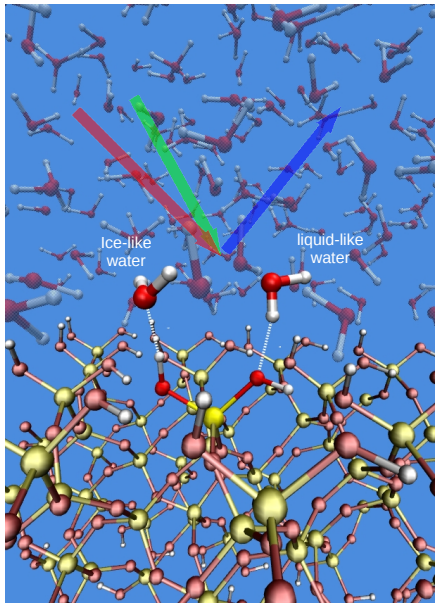
Special Issue hosted by Sulpizi, Gaigeot (2012, 2014) Exps+Simulations

DFT-based MD simulations @ finite temperature is the good way to investigate structure, dynamics & spectroscopy



Exps. Shen et al. (USA)

DFT-MD of oxides/water interfaces



- Structural organisation of the water at the interface with the oxide surface
- Dynamics of water at the interface
- Influence of the water on properties of the oxide surface
- pKa of surface sites
- Spectroscopy of water at the interface
  Interpretation/Assignments of VSFG experiments from detailed microscopic features

2 interfaces investigated :

- Silica oxide / water interface
- Alumina oxide / water interface

Neutral pH conditions, Surfaces fully hydroxylated
(charged surfaces under investigation)

Coll. M. Sulpizi (Mainz, Germany), M. Sprik (Cambridge, UK),
J. Phys. Cond Matter 2012, J.C.T.C. 2012

Organisation of CECAM Workshop 2011 & 2013 + Special Issues J.Phys.Cond. Matter on Solid/Liquid Interfaces (2012, 2014)

DFT-MD of Solid oxides/water interfaces

Coll. M. Sulpizi (Mainz, Germany), M. Sprik (Cambridge, UK),
J. Phys. Cond Matter 2012, J.C.T.C. 2012

CP2K package, BOMD, BLYP, 400 atoms in the cell, 330 K

α-quartz Surface (0001)

α-quartz : (0001) hexagonal Surface

Supercell : 9.820 X 8.504 X 22.300 $Å^3$

Fully hydroxilated surface

400 atoms simulated

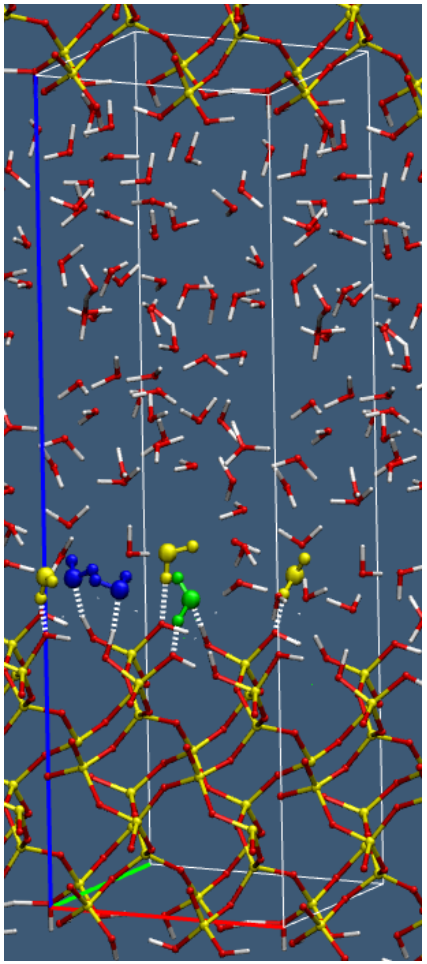
α-alumina Surface (0001)

α-alumina (corundum) : R-3c space group

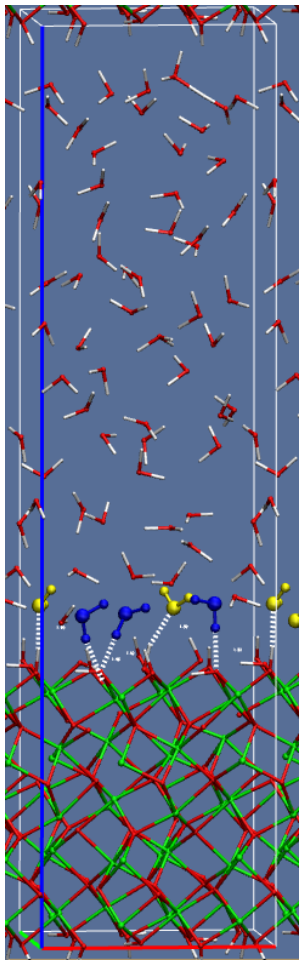
Supercell : 9.514 X 8.239 X 25.237 $Å^3$

Fully hydroxilated surface

400 atoms simulated

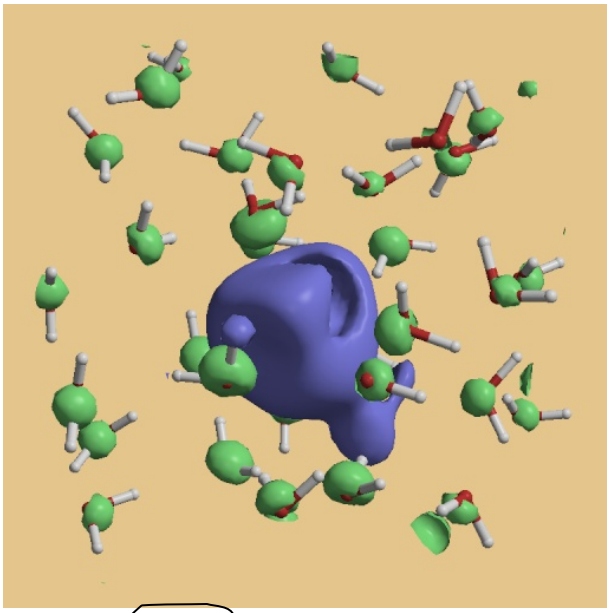


silica/water interface



alumina/water interface

ab-initio Molecular Dynamics



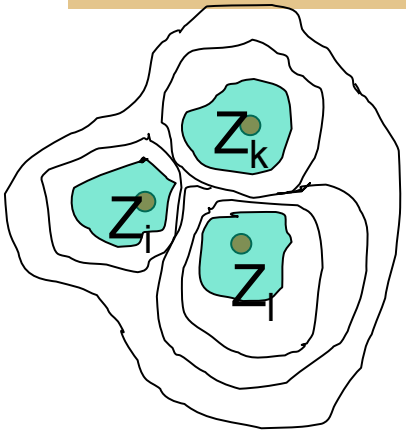
$$H\,\Psi(\vec{r}\,,\vec{R}\,) = E_0(\vec{R}\,)\,\Psi(\vec{r}\,,\vec{R}\,)$$

$$\mathcal{L}(\vec{R}\,,\vec{P}\,) = \sum_i \frac{\vec{P}_i^{\,2}}{2\,M_i} - E_0(\vec{R}\,)$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = 0$$

BO approximation
Schrödinger equation

Newton/Lagrange dynamics



Classical nuclei

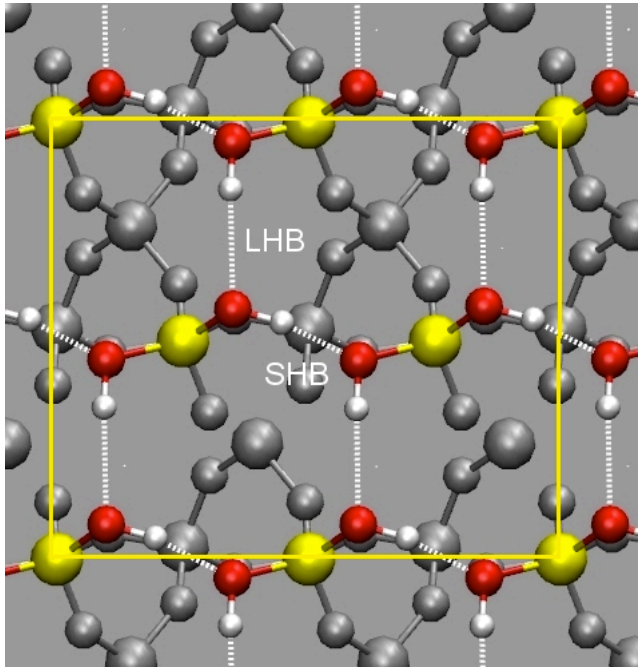
Electronic clouds

Two approaches in the DFT framework :
Born-Oppenheimer MD (CP2K code) & Car-Parrinello MD (CPMD code)

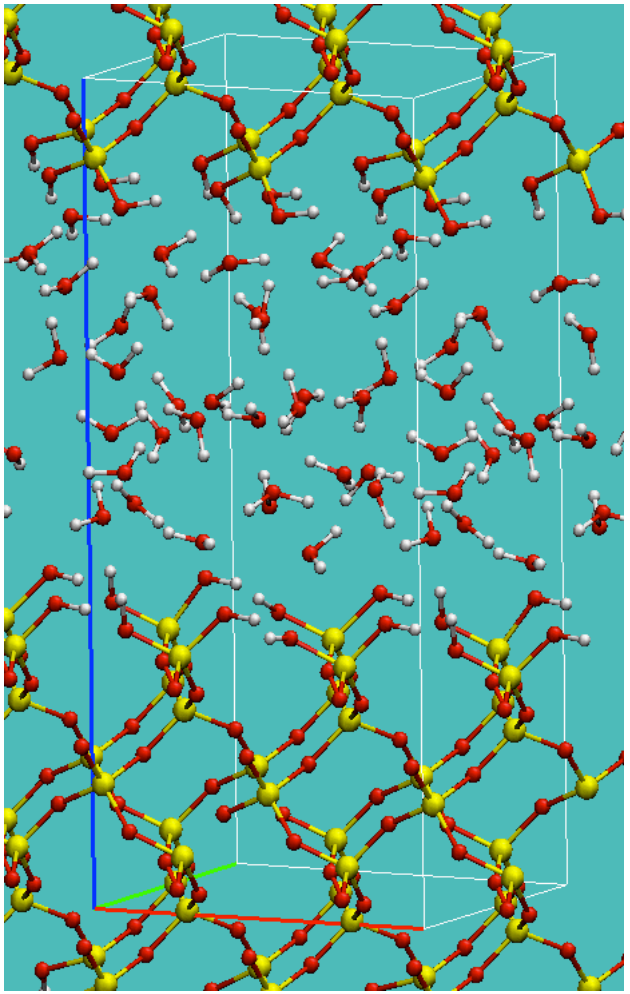
Use of Wannier Centers in order to calculate molecular dipoles (IR)
& molecular polarisability tensors (Raman, SFG)

100' atoms - 10' pico-seconds

α-quartz Surface (0001) : Water influences the surface hydroxyls organisation



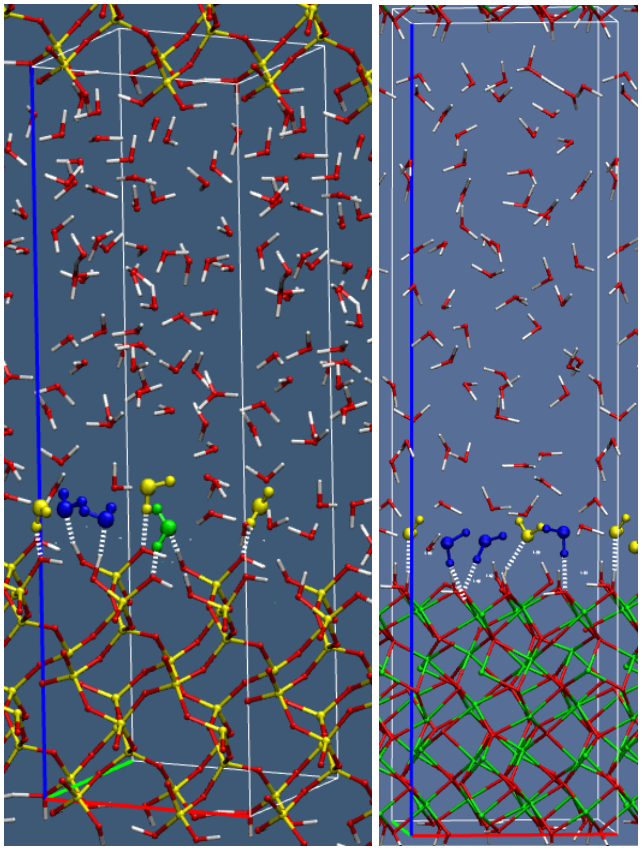
Dried surface : In-plane zig-zags of H-bonds between hydroxyl groups



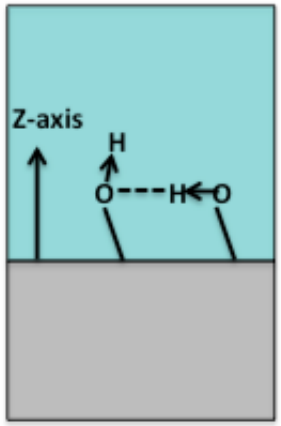
Wet surface : In-plane Si-OH and Out-of-plane Si-OH now exist and alternate - Both are interacting with liquid water at the interface (1st layer of solvent above the surface)

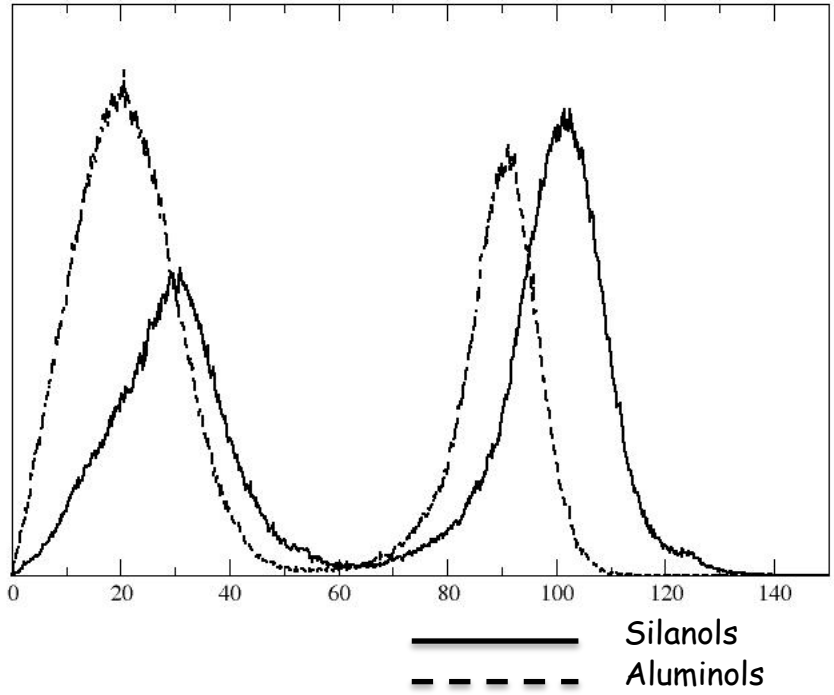
(…. same for alumina …)

Organisation of surface O-H groups at solid interfaces : silica oxide/ and alumina oxide/ water interfaces



silica/water interface alumina/water interface





Bimodal distributions for the two oxide/water interfaces

1 Peak : O-H in the plane of the surface

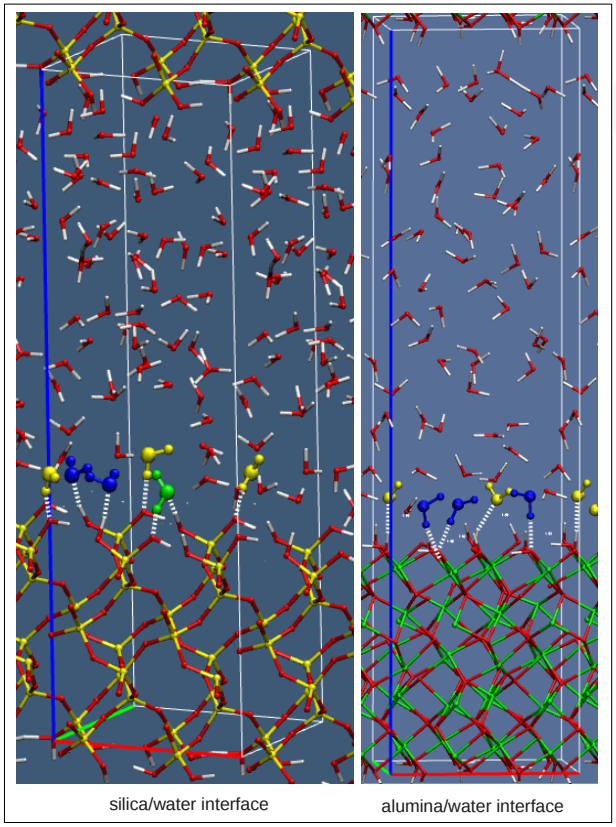
1 Peak : O-H out of the plane of the surface, pointing towards the water

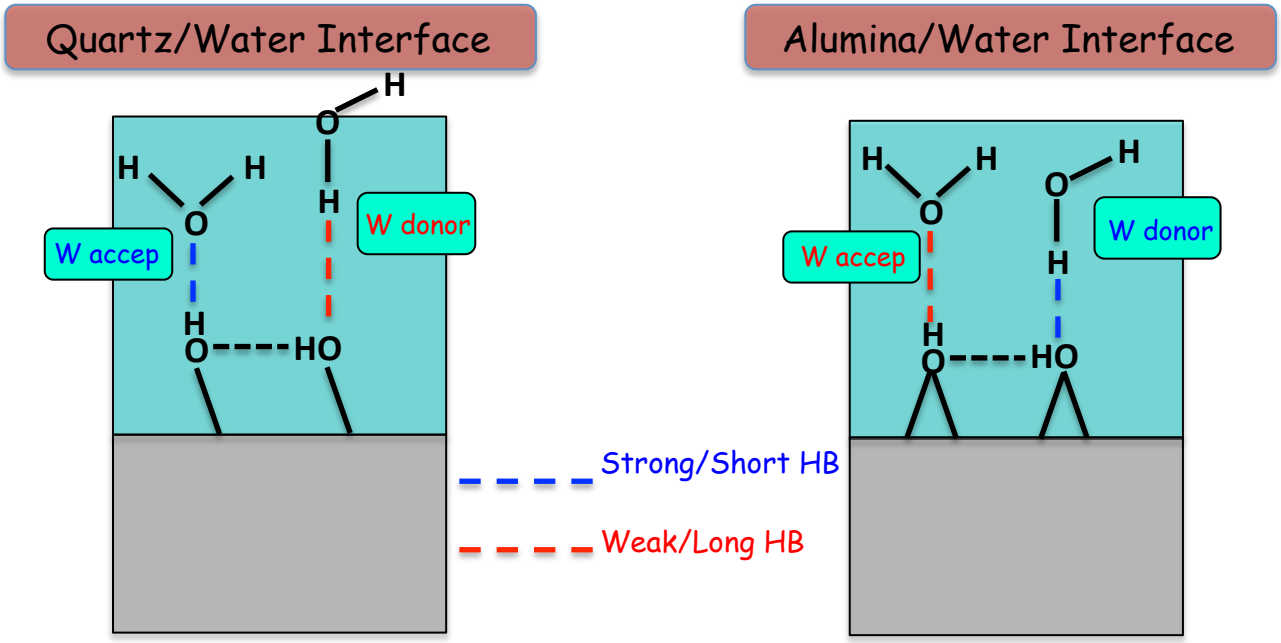
Both orientations are alterning along the surface

In-Plane Si(Al)-OH → intramolecular hydrogen bonds within the surface

Out-of-Plane Si(Al)-OH → intermolecular hydrogen bonds between surface hydroxyls and water

Hydrogen bonds between water (first layer) and surface : silica oxide/ and alumina oxide/ water interfaces





Water H-Bond donors ←→ In-Plane surface hydroxyls

Water H-Bond acceptors ←→ Out-of-Plane surface hydroxyls

Water Donor/Acceptor alternate at the interface because of the alternate nature of In-Plane/Out-of-Plane surface hydroxyls

Majority of Water molecules then interact with 2nd shell Water

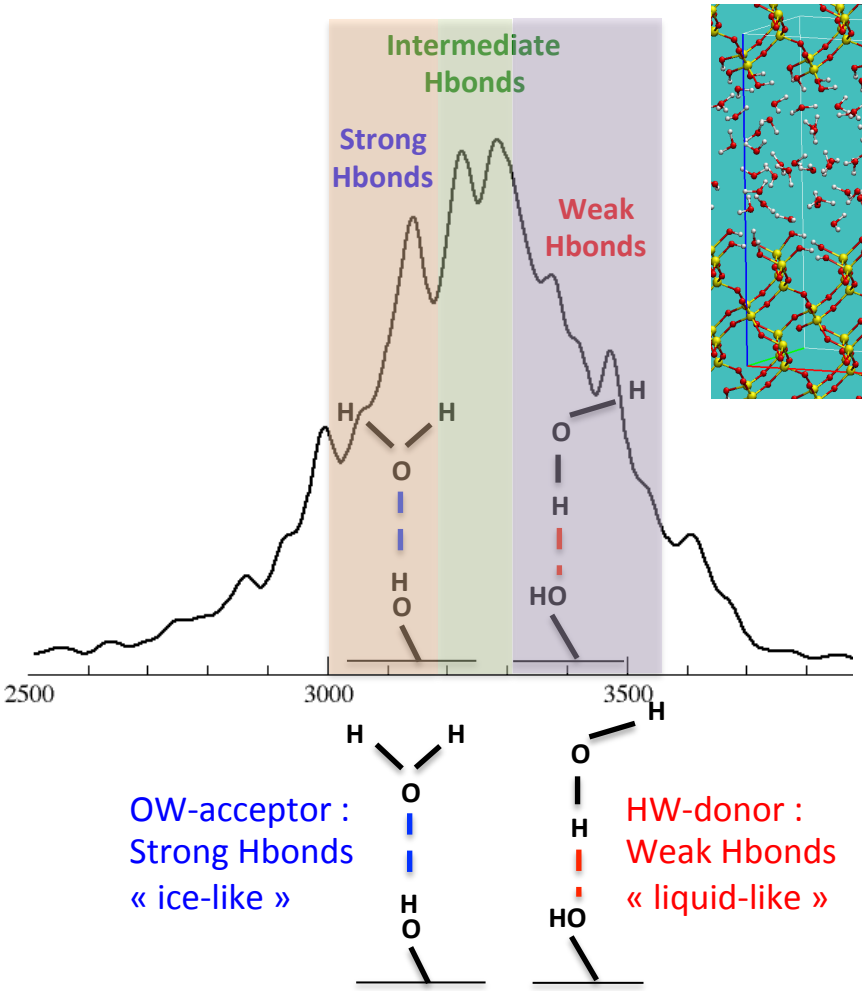
4 HB : 1 H B with surface + 3 HB with water from the 2nd shell
(4.3 HB for Quartz/Water and 4.1 for Alumina/Water)

Possibility of transient Water-Water Hbonds within the 1st layer

Vibrational IR signatures of water at solid/liquid interfaces

$$I(\omega) = \alpha(\omega) n(\omega) = \frac{2\pi\omega\left(1 - e^{-\beta h\omega}\right)\mathcal{D}(\omega)}{3hcV} \int_{-\infty}^{+\infty} \mathrm{dt} \left\langle \vec{M}(t).\vec{M}(0) \right\rangle e^{i\omega t}$$

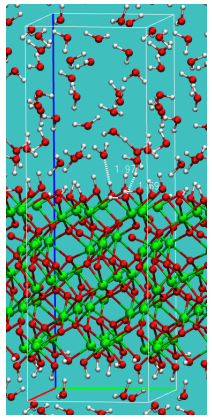
Interface Quartz/liquid water



OW-acceptor :
Strong Hbonds
« ice-like »

HW-donor :
Weak Hbonds
« liquid-like »

Interface Alumina/liquid water



HW-donor :
Strong Hbonds
« ice-like »

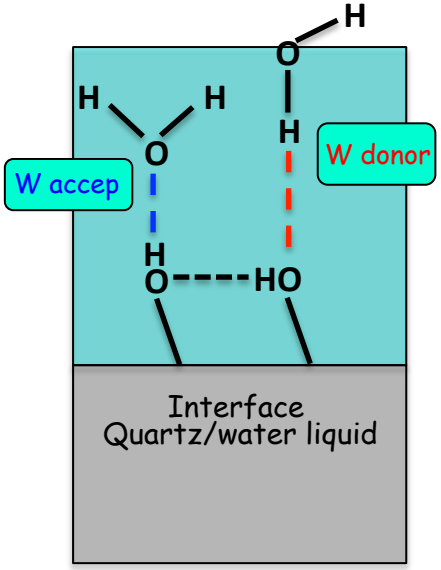
OW-acceptor :
Weak Hbonds
« liquid-like »

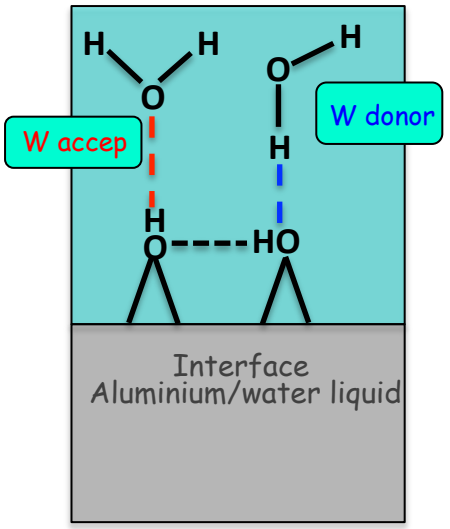
Reversal of H-bond signatures between the two interfaces : donor/acceptor - weak/strong H-bonds

→ Interpretation of SFG signatures from DFT-MD of the interfaces (true signal under calculation)

pKa calculations of surface sites : silica oxide/ and alumina oxide/ water interfaces

(method of M. Sprik, M. Sulpizi, PCCP 2008, JCP 2009, JCP 2011)





pKa of Silanols : 5.6 (our calculation)

Acidic
Easily releases a proton in solvent
➔ Strong Hbond with water

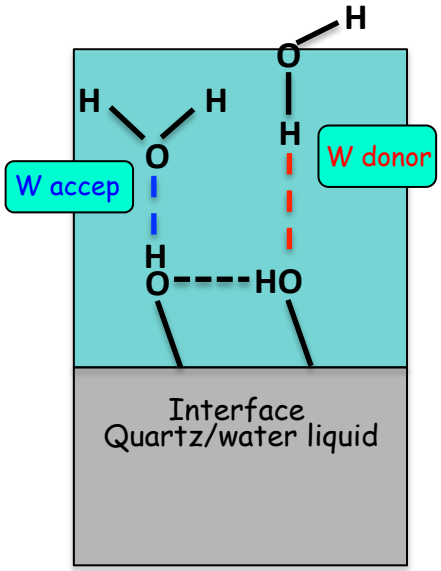
pKa of Aluminols : 16.6 (our calculation)

Basic
Does not easily release a proton in solvent
➔ Weaker Hbond with water

Structural properties/HBonds of first interfacial layer are consistent with pKa values of surface hydroxyl groups at the interface

Acid/Basic characters of Silanols/Aluminols determine/« dictate » the arrangement of the water molecules Hbonded to the surface and modulate the water properties

pKa calculations : special case of the silica oxide/water interfaces
The bimodal behaviour interpreted



pKa of Out-of-Plane Silanols : 5.6 (our calculation) (Exp: 4.5)

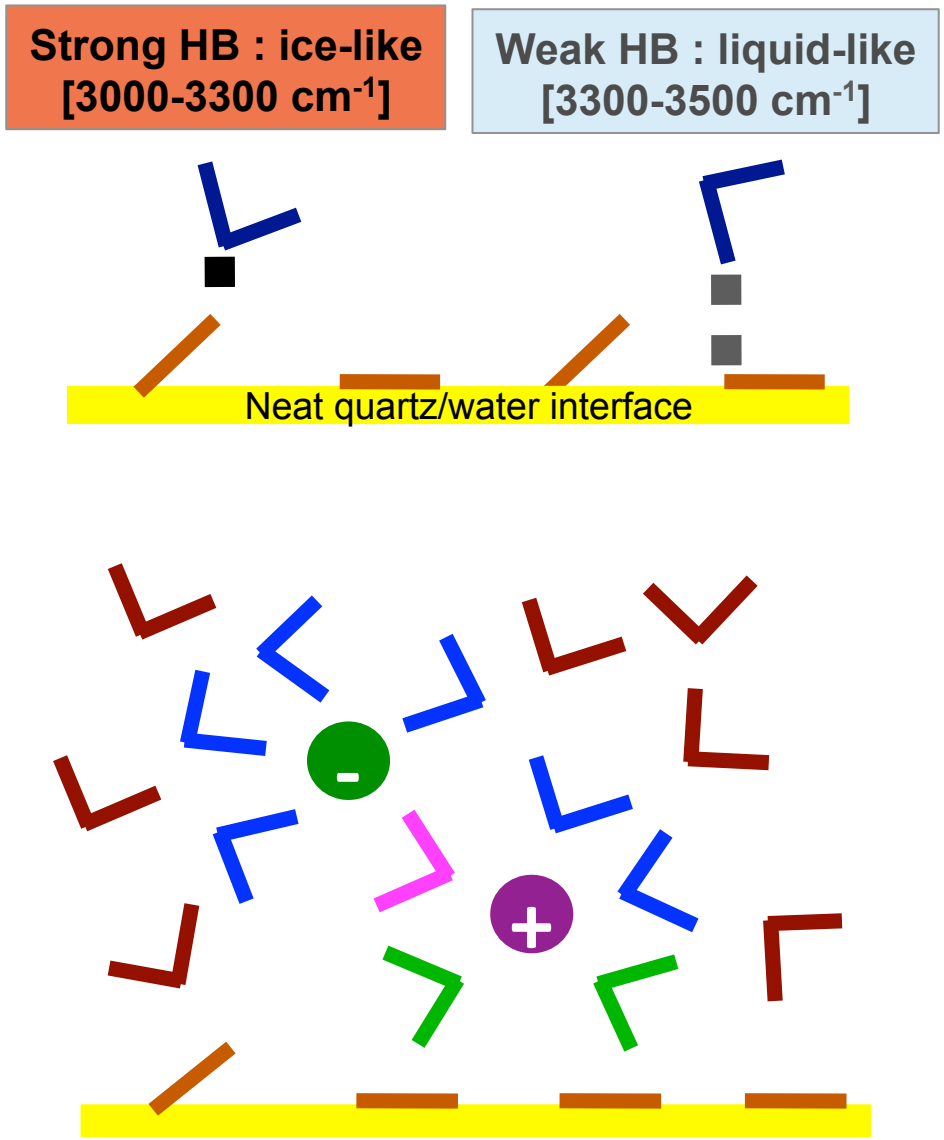
pKa of In-Plane Silanols : 8.5 (our calculation) (Exp: 8.5)

Bimodal behaviour of the 2 Silanols at the interface

Experiments → Bimodal behaviour (Shen PRL 1985, Eisenthal CPL 1992)

PZC = 1.0 (Calc.) [2-4 Exps]

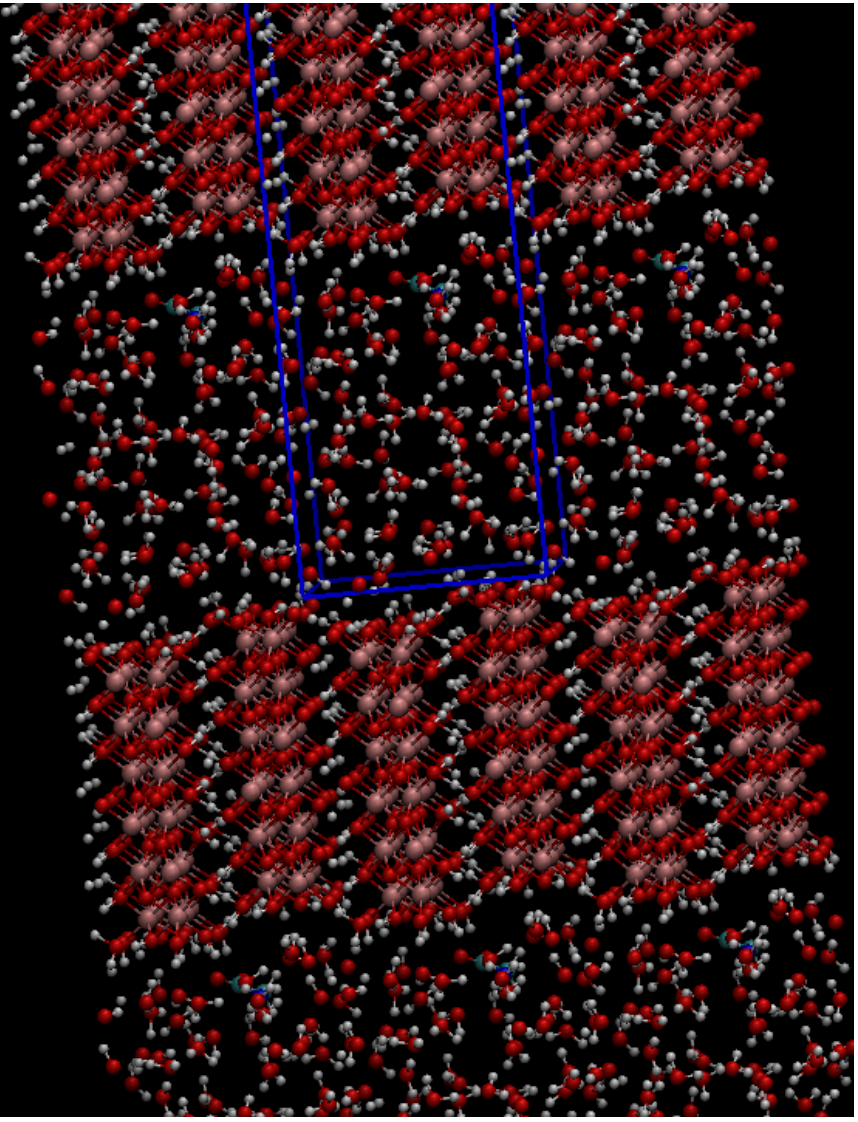
Adsorbed ion pairs (0001) at the α-quartz/water interface

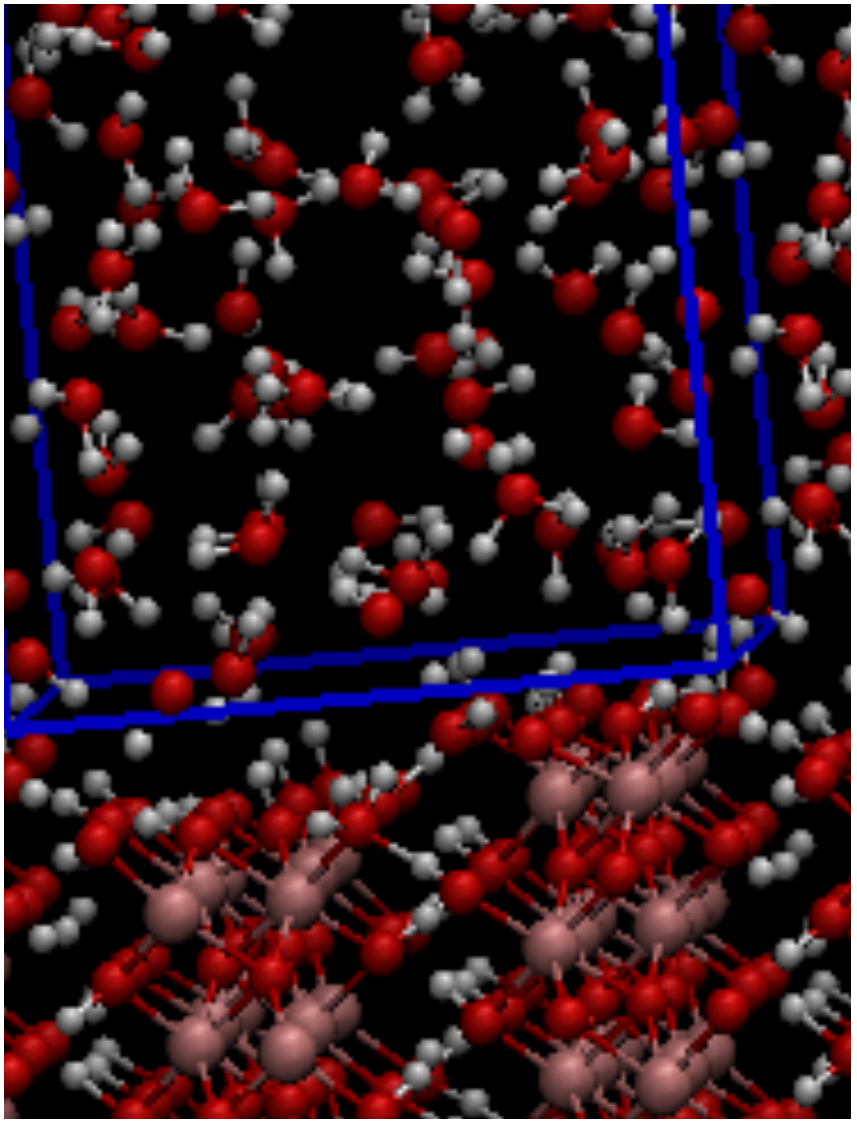


- 3 solvent separated ion pairs : NaI, NaCl and Kcl
- Ion pairs : conformational dynamics.
  Most dynamical system: NaCl
  Less dynamical system: KCl
- Perturbed silanols : they are kept in-plane by cations + ratio IP/OP increasing from NaI-NaCl to KCl
- Ion solvation shells : as in bulk water
- VDOS signatures : OH from interfacial silanols and OH from water molecules forming the different ion solvation shells (colors on the figure)

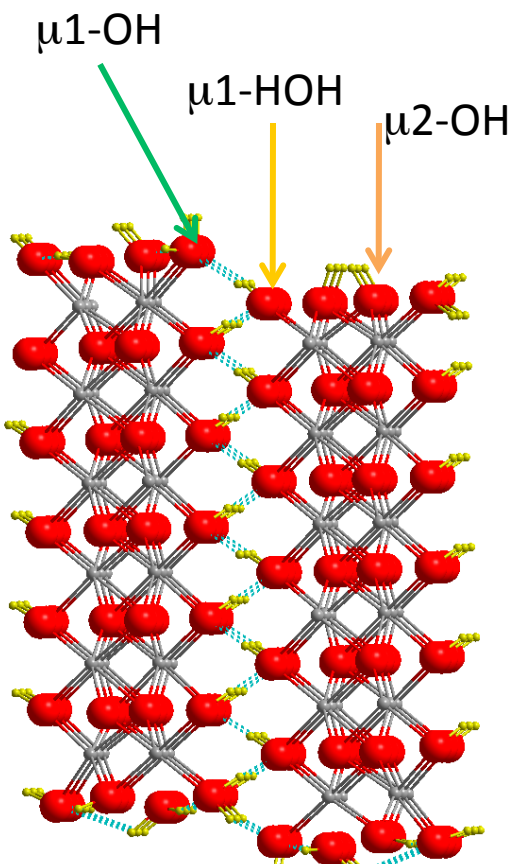
Boehmite (101) AlOOH/Water Interface

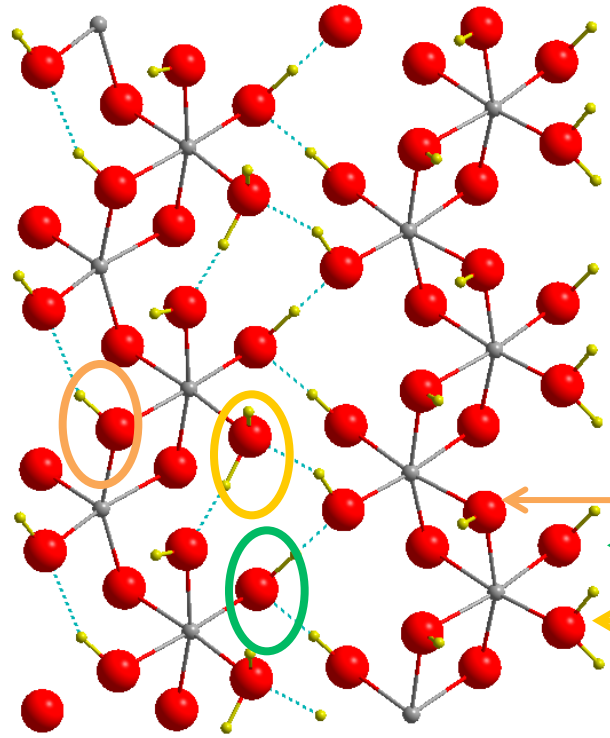
Motta, Gaigeot, Costa, JPCC 2012 (116:12514, 116:23418)

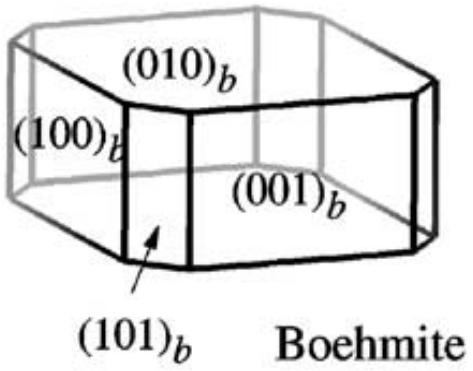




Boehmite (101) step surface





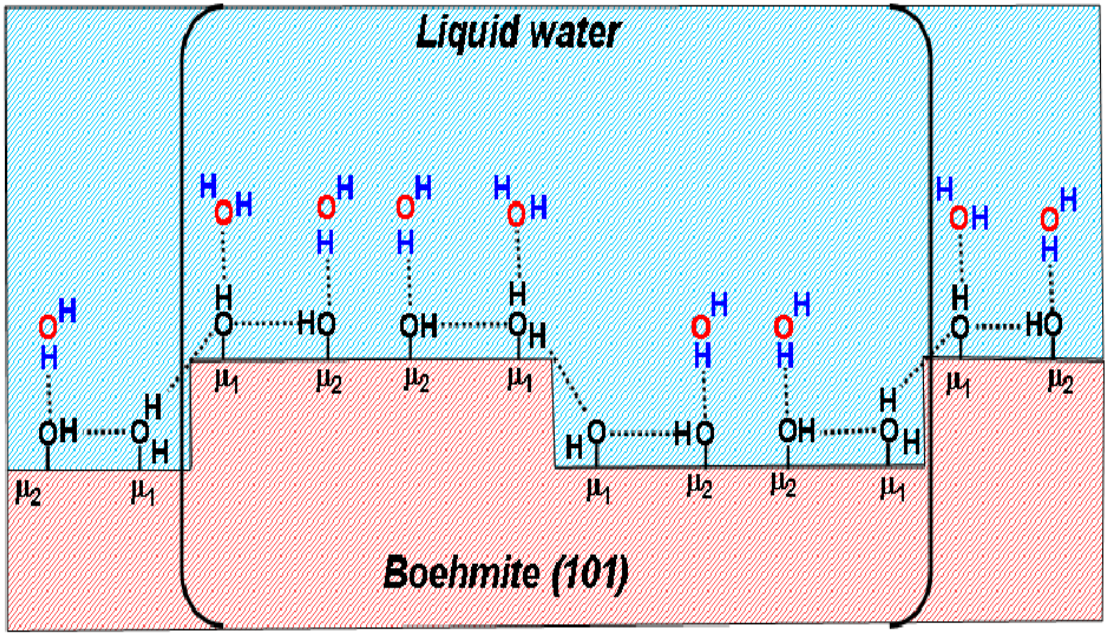


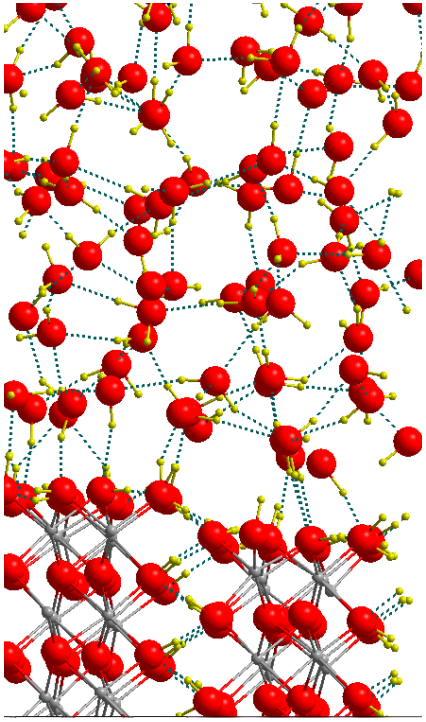
Thermodynamics calculations: fully hdroxylated
Three types of OH groups
Music's charge zero
pZc of boehmite 8-9

The Calculated Proton Association Constants for Several Important Surface Reactions at Various Important (Hydr)oxides[a]

Surface group	Formal charge	log *K*	*L*
Al–OH	$-\frac{1}{2}$	10.0	2.59
Al_2–O	−1	12.3	2.43
Al_2–OH	0	−1.5	2.43
Al_3–O	$-\frac{1}{2}$	2.2	2.49

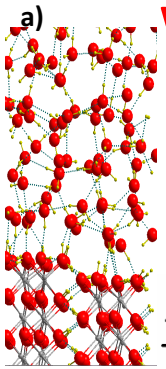
HBond networks @ finite temperature

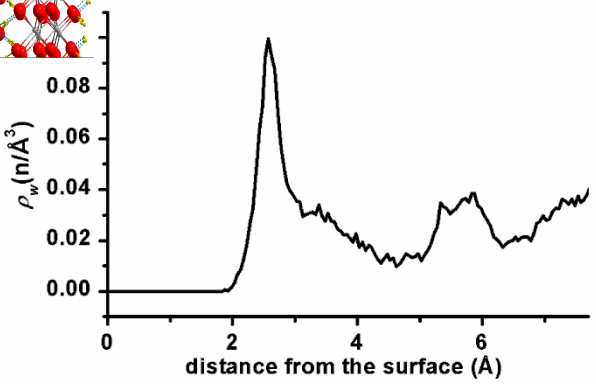


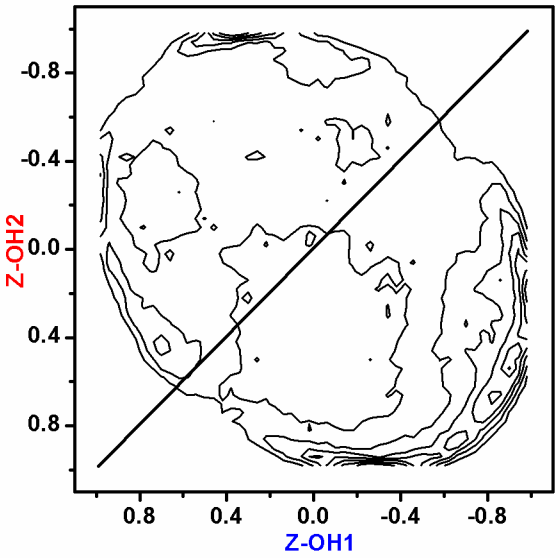


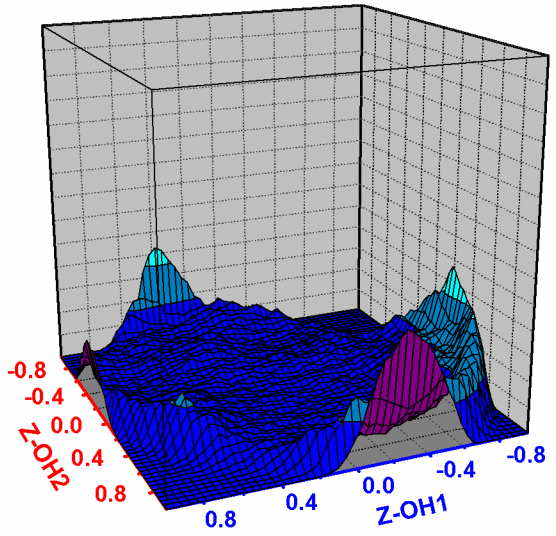
H-bond network between the aluminols within the surface
& H-bond network between the aluminols and water at the interface

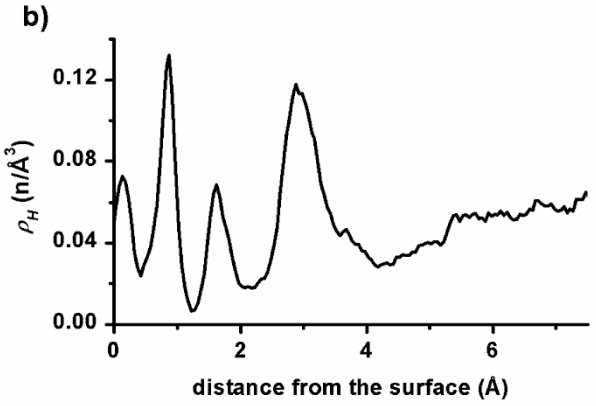
Water @the boehmite Interface: specific orientations

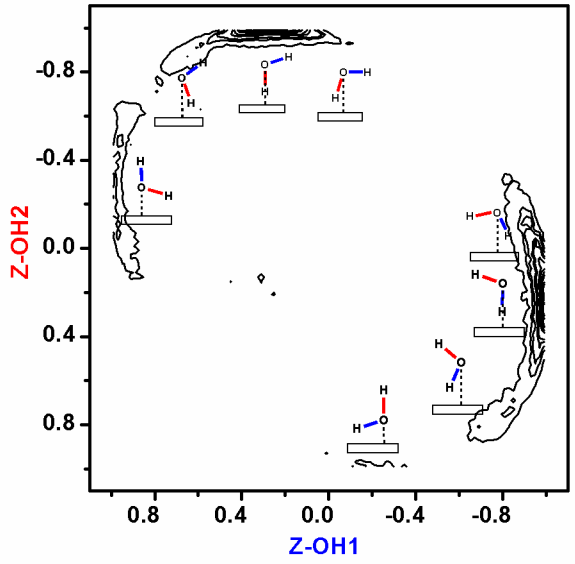


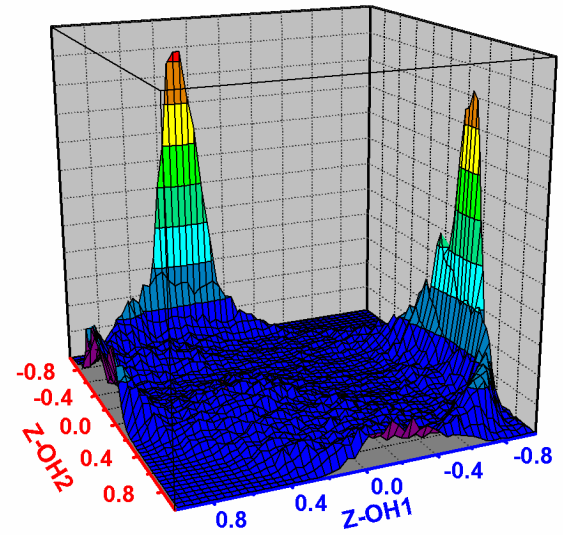






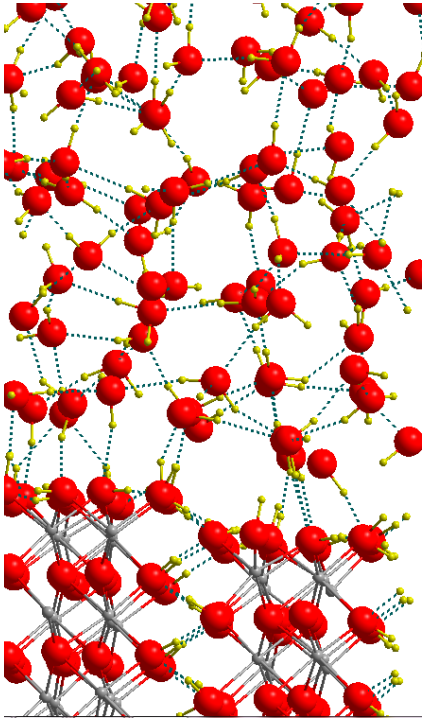


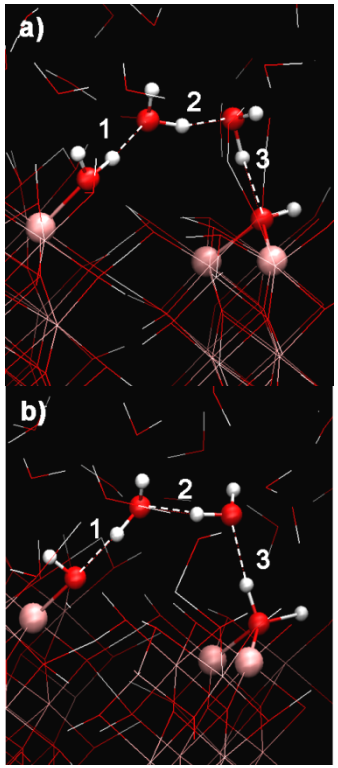




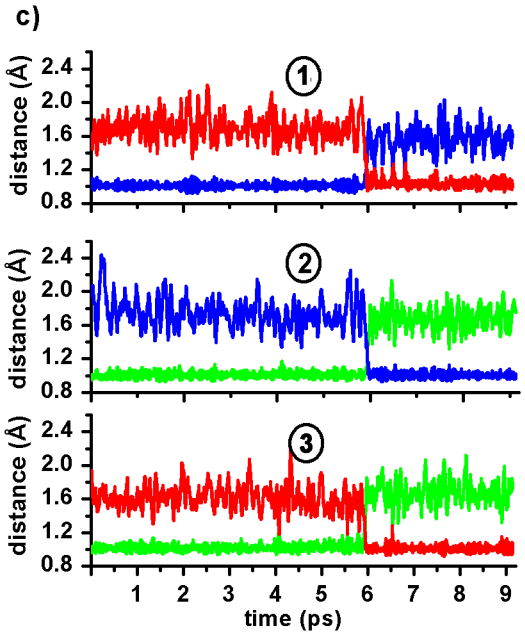
Motta, Gaigeot, Costa, JPCC 2012 (116:12514, 116:23418)

Protonic Conductivity@the step





Grotthus mechanism for H exchange



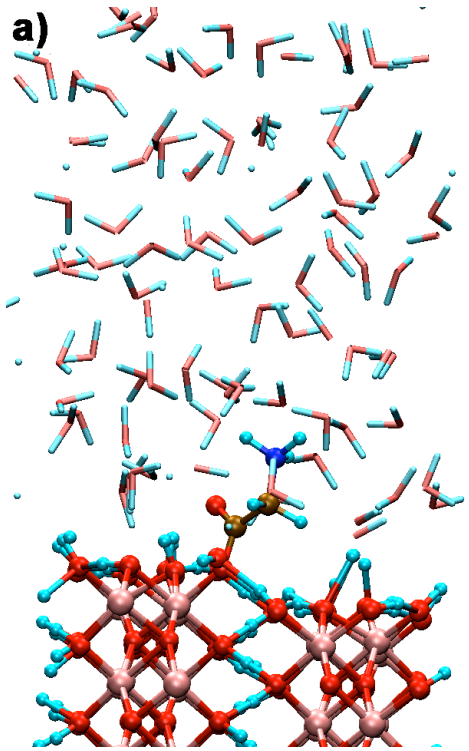
μ1-HOH + μ2-OH ⇌ μ1-OH + μ2-HOH ΔpK(μ1-OH) = 1.4

MUSIC predicts 2-3 units pK difference (Jolivet et al 2004)

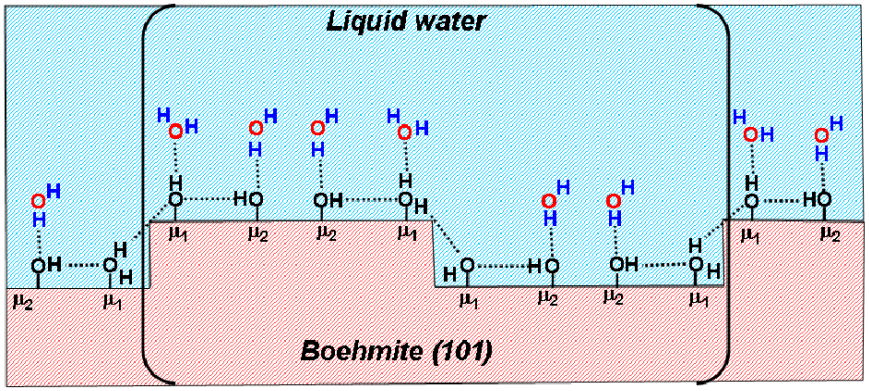
DFT-MD of boehmite/water interface and the adsorption of glycine

Coll. D. Costa (ENSCP ParisTech), JPCC 2012 (116:12514, 116:23418)

CP2K package, BOMD, BLYP + D2, 640 atoms in the cell, 330 K
Supercell : 14.05 X 11.70 X 32.4845 $Å^3$

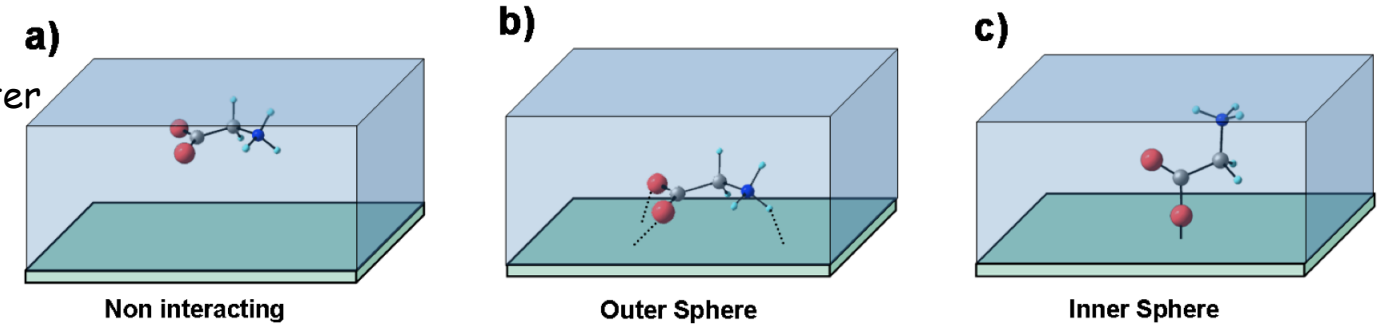


Hydroxylations of boehmite at the aqueous interface
& organisation of interfacial water molecules
(JPCC 2012 116:12514)

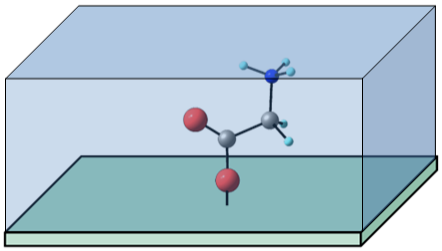


Energetically most favorable adsorption mode of Glycine at the aqueous boehmite/water interface ?

(JPCC 2012 116:23418)

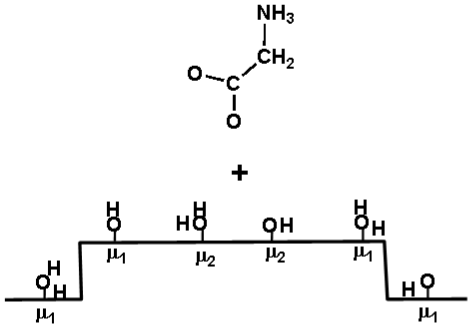


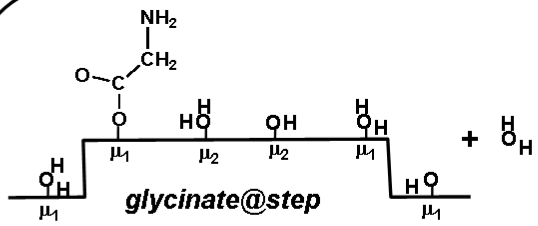
c)

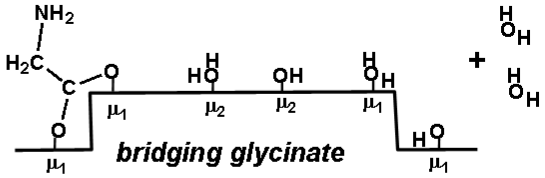


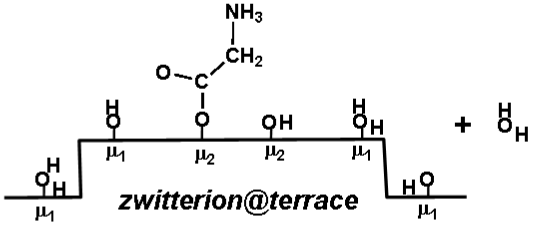
Inner Sphere

Several condensation reactions of Glycine COO^- termini with the different Al surface sites

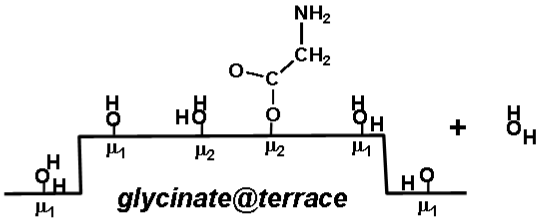


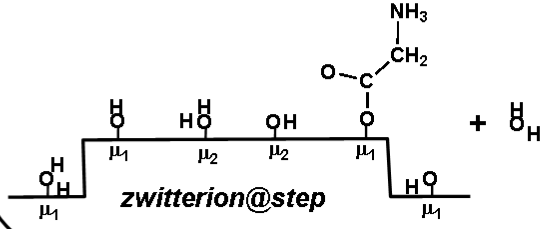




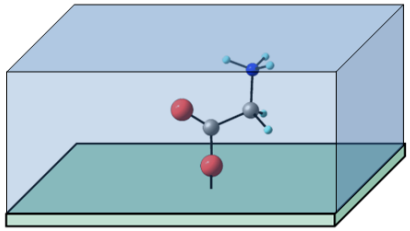


DFT-MD investigate all possibilities





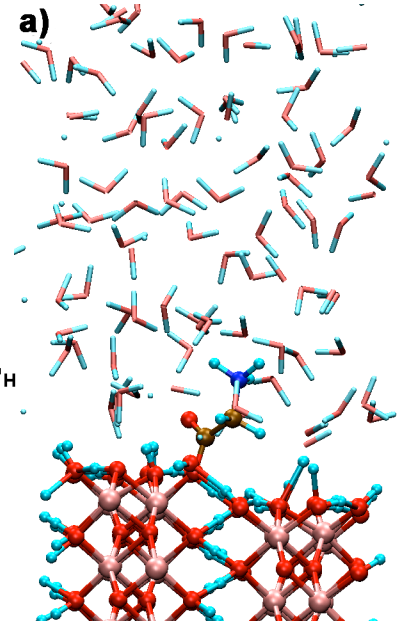
c)



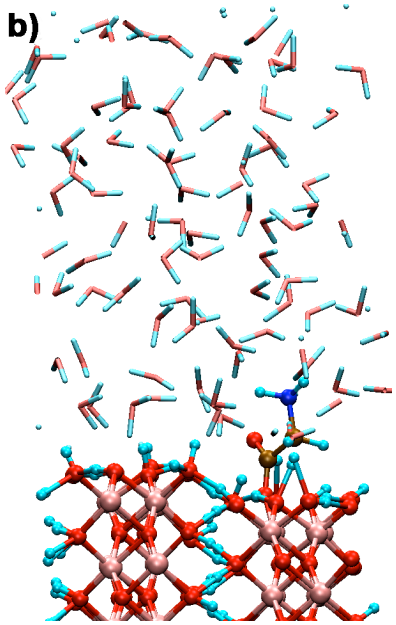
Inner Sphere

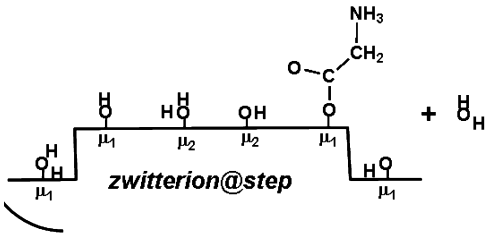
The two most stable structures: inner-sphere adsorption

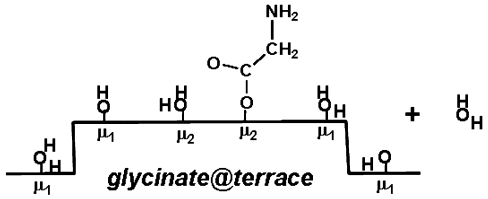
a)



b)







< ΔE^{KS} > = -113.6 kJ/mol

< ΔE^{KS} > = -161.3 kJ/mol

(taking into account the organisation of interfacial water ; Eref=Gly in liquid phase, non-interacting)

Average view :

$NH_3^+(NH_2)$ Hbonded to 3(2) H_2O ; 1 COO Hbonded to mu2-OH or mu1-OH

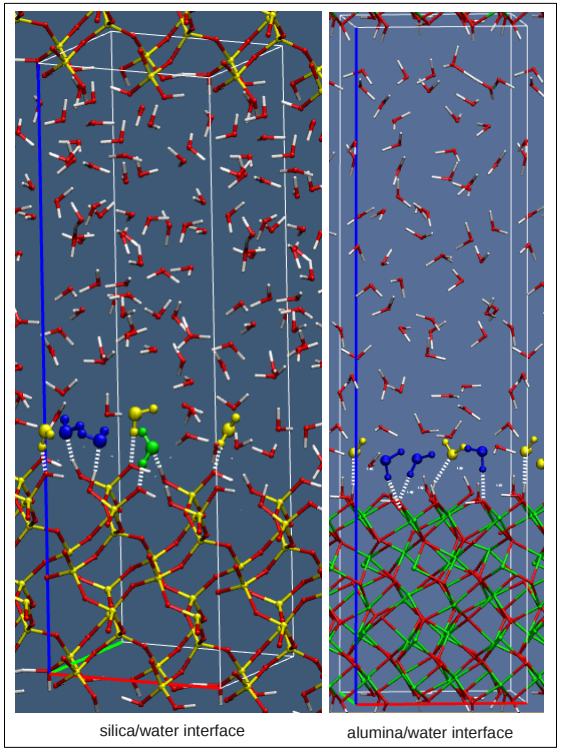
Outer-sphere conformation: -20.5 kJ/mol

- DFT-MD of Quartz/water & Alumina/water interfaces :

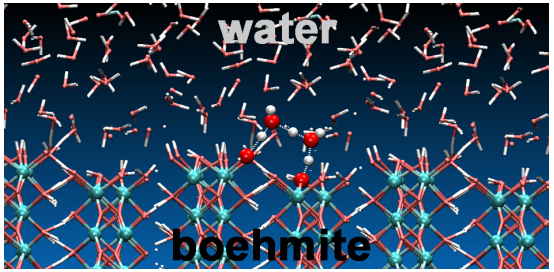
  Liquid structure, solid structure, pKa, IR spectra

  Full VSFG spectrum currently calculated from DFT-MD

  Coll M. Sulpizi, M. Sprik JCTC 2012, J.Phys.Cond.Matt 2012



- Boehmite/Water interface (Coll. D. Costa, Paris)



- Proton transfers at the step
- Peptides @ the interface

JPCC(1) 2012, + JPCC(2) 2012

- VSFG signal of liquid water/air interface
  DFT-MD, JPCLetters 2013

- Electrolytes or peptides at the interface

Collaborators on these works :

Morgane Pfeiffer (PhD, 2012-2015)

Alvaro Cimas (MdC Evry France)

Michiel Sprik - Cambridge UK

Marialore Sulpizi - Mainz Germany

Dominique Costa - ENSCP France, Alessandro Motta, Italy
Mathieu Salanne – UPMC Paris France

Group of M Bonn & E Backus – Max Planck Institute Mainz, Germany

Group of J. Gibbs-Davis – University of Alberta, Canada

Group of J. Lisy – University of Urbana Champaign, Illinois, USA